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RESEARCH LETTER

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Key Points:

- Dolomite formation is not directly controlled by water temperature, Mg/Ca ratio, salinity, pH, alkalinity, or amount of biomass
- Cyclic occurrence of dolomite in sediments of deep alkaline Lake Van is controlled by orbital and suborbital climate variability
- Paleoenvironmental reconstructions based on factors commonly considered crucial for dolomite formation may require reevaluation

Supporting Information:

- Supporting Information S1
- Data Set S1

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Controls on Cyclic Formation of Quaternary Early Diagenetic Dolomite

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Abstract The origin of sedimentary dolomite and the factors that control its formation within the geological record remain speculative. In most models, dolomite formation is linked to evaporative conditions, high water temperature, increasing Mg/Ca ratio, increasing alkalinity, and high amounts of biomass. Here we challenge these archetypal views, by documenting a case example of Quaternary dolomite which formed in Lake Van at constantly low temperature (<4°C) and without direct control of the latter conditions. Dolomite occurs within highstand sediments related to suborbital climate variability (Dansgaard-Oeschger cycles). We propose that dolomite precipitation is a product of a microbially influenced process, triggered by ecological stress, resulting from reventilation of the water-sediment interface. Independently from the validity of this hypothesis, our results call for a reevaluation of the paleoenvironmental conditions often invoked for early diagenetic dolomite-rich intervals within sedimentary sequences and for caution when interpreting time series of subrecent lacustrine carbonates.

Plain Language Summary The mineral dolomite is a common constituent of many ancient rock formations, including important hydrocarbon reservoirs and sedimentary sequences that are studied for paleoclimatic reconstructions. Because dolomite is very difficult to precipitate in laboratory experiments that simulate Earth's surface conditions, the key factors controlling its occurrence in the geological record remain speculative and debated. Through the study of subrecent sediments recovered from a deep alkaline lake, we show that warm and evaporitic conditions, as well as other factors commonly considered crucial for dolomite formation, are not as essential as traditionally thought. Consequently, the interpretation of several dolomite-rich sedimentary sequences may require a substantial re-evaluation.

1. Introduction

Modern dolomite-forming environments are mainly represented by sabkhas, playa lakes, and hypersaline lagoons. Studies of these evaporitic settings have led to the formulation of several models commonly used for interpreting ancient sedimentary sequences rich in dolomite (Petrash et al., 2017), including rocks that are relevant for understanding the evolution of early life (Allwood et al., 2009) and others that constitute economically important oil and gas reservoirs (Alsharhan & Kendall, 2003). In most models, high fluid temperatures, high Mg/Ca ratios, and high alkalinity are considered key factors for dolomite formation (Machel, 2004; Warren, 2000). Accordingly, the presence of dolomite within the late glacial sediments of alkaline Lake Van (Turkey) has been unanimously associated with periods of enhanced evaporation, a high Mg/Ca ratio, and either low lake levels or complete desiccation (Degens et al., 1984; Landmann et al., 1996; Lemcke & Sturm, 1997). Also in a more recent work (Çağatay et al., 2014), the sporadic occurrence of dolomite in last glacial sediments and the interval related to the Younger Dryas cooling has been associated with arid conditions.

We systematically analyzed the sedimentary record of Lake Van covering the last 150 ka before present (BP) documenting recurring (cyclic) high concentrations of dolomite. The nature of our material does not allow for assessing the possible, and recently hotly debated, role of very high Mg calcite precursor phases in early diagenetic (nonstoichiometric) dolomite formation (Gregg et al., 2015; Petrash et al., 2017). Instead, it provides a unique opportunity for testing the envelope of environmental conditions assumed essential for dolomite formation. If juxtaposed with environmental proxies reflecting regional and local hydrological conditions (Kwiecien et al., 2014; Litt et al., 2014; North et al., 2017; Pickarski, Kwiecien, Djamali, et al., 2015; Pickarski, Kwiecien, Langgut, et al., 2015; Pickarski & Litt, 2017; Randlett et al., 2017; Stockhecke, Sturm, et al., 2014; Tomonaga et al., 2017) (Figure 1), the dolomite occurrence is incompatible with the commonly accepted hypothesis of evaporitic conditions driving its formation. Our high-resolution dolomite

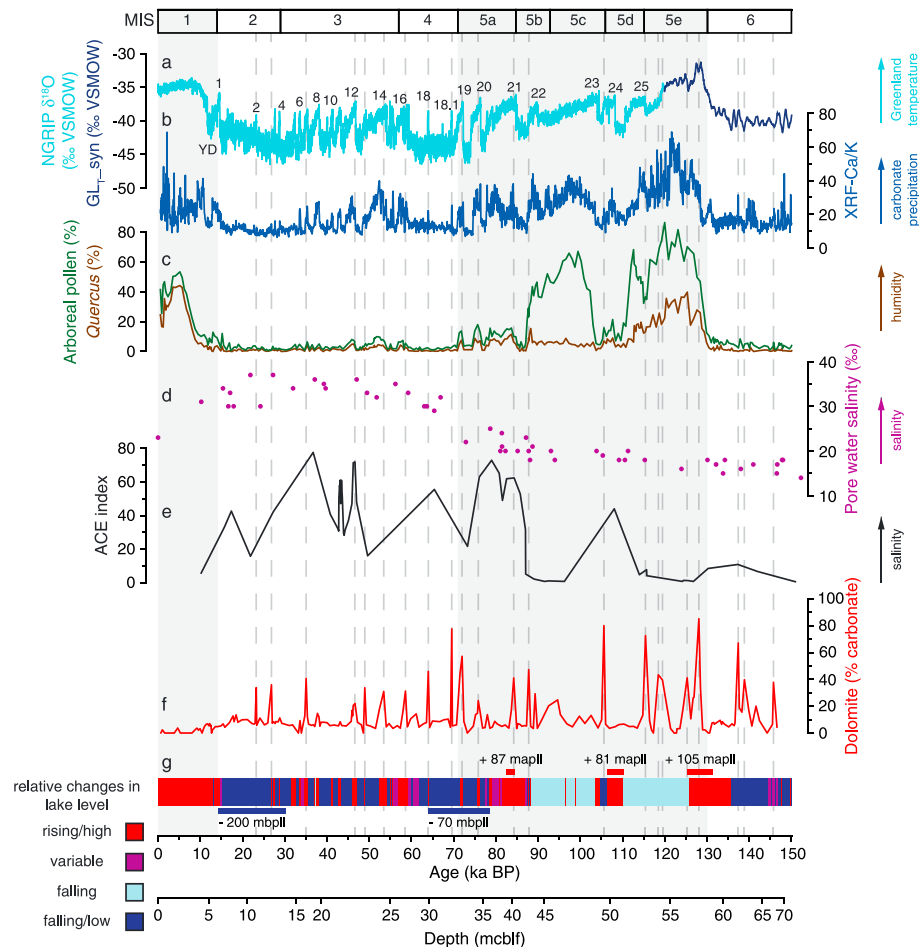


Figure 1. Lake Van dolomite distribution compared to proxies of relative moisture availability, salinity and lake level. (a) Isotopic composition of NGRIP ice core (NGRIP, 2004; Steffensen et al., 2008; Svensson et al., 2008; Wolff et al., 2010) and synthetic isotopic composition of Greenland ice (GLT_{syn}) (Barker et al., 2011) are depicted as reference curves with the Younger Dryas (YD) marked and numbered Greenland Interstadials. Sedimentary proxies from Lake Van include (b) XRF-Ca/K ratio (Kwiecien et al., 2014), (c) arboreal pollen and *Quercus* pollen percentage (Litt et al., 2014; Pickarski, Kwiecien, Djamali, et al., 2015; Pickarski, Kwiecien, Langgut, et al., 2015; Pickarski & Litt, 2017), (d) pore water salinity plotted against depth in meter composite below lake floor (mcbf; Tomonaga et al., 2017), (e) biomarker Archaeol and Caldarchaeol Ecometric (ACE) index (Randlett et al., 2017), and (g) lithologies with genetic interpretations related to lake-level variability as colored bar (Stockhecke, Sturm, et al., 2014) and major lake-level variations (Stockhecke, Sturm, et al., 2014; Tomonaga et al., 2017) in meter above/below present lake level (mapl/mbpl). (f) Dolomite concentration is given in % of relative carbonate concentration. The grey shaded areas represent interglacials.

concentration data (Figure 1), presented on the common Lake Van age model (Stockhecke, Kwiecien, et al., 2014), suggest that most of the dolomite-rich intervals coincide with sediments deposited during a high lake level and generally wetter conditions. These wetter phases are also documented in other climate archives across the Eastern Mediterranean region (e.g., Rowe et al., 2012; Stevens et al., 2012). Such conditions are usually not expected to favor dolomite formation; hence, we reconsider Lake Van as an exceptional site for evaluating the factors that control the formation of dolomite and its uneven distribution throughout the geological record.

2. Methods

This study was carried out on material recovered in 2010 as part of the International Continental Scientific Drilling Program PALEOVAN. We resampled the Ahlat Ridge composite profile and off-section. Visual correlation based on high-resolution images allowed assigning composite profile depth (and age; Stockhecke, Kwiecien, et al., 2014) to off-section samples. The data presented here comprise 216 samples (single sample resolution of 2 cm) from the uppermost 67 m (55 m without event deposits, mcbf-nE) of the composite profile corresponding to 146.6 ka BP. Samples were wet-sieved with distilled water through a succession of

sieves with a minimum mesh size of 63 μm . The <63 μm fraction was decanted through filter paper and air-dried at room temperature. For X-ray powder diffraction (XRD) and stable isotope analysis an aliquot of each dried sample was homogenized with an agate mortar. Material from the not homogenized aliquots as well as oven dried (50°C) bulk material was used for scanning electron microscopy (SEM). SEM analysis was performed on gold-coated samples using a LEO/Zeiss Gemini 1530 operating with an acceleration voltage of 20 kV. Identification of chemical mineral composition was archived by the use of the energy-dispersive X-ray spectroscopy system and the AZtec software package from OXFORD Instruments.

XRD analysis was performed on a PANalytical Empyrean equipped with a PIXcel1D detector using Cu K_{α} radiation, applying a tube voltage and current of 45 kV and 40 mA, respectively. Operating conditions included a step size of 0.0131° and a counting time of 3 s per step for 2θ from 4 to 65°, fixed 0.25° divergent, and 0.5° antiscatter slits in the incident beam path, incident and diffracted beam 0.04 rad soller slits, and a 7.5-mm high antiscatter slit together with a Ni filter in the diffracted beam optics. Mineral identification and semi-quantitative estimation of dolomite relative to other carbonate phases (aragonite, calcite) and bulk sediment were performed with the PANalytical X'Pert HighScore Plus software and based on mineral Relative Intensity Ratios. Concentration of dolomite relative to bulk sediment was further visually controlled by SEM imaging of selected samples. A fully quantitative mineralogical analysis is compromised here by the complexity of the mineral assemblage (e.g., high number of mineral phases, inhomogenic nature of clay, and feldspar minerals). The degree of dolomite cation ordering was determined from the intensity ratios of the ordering peak 015 to the 110 peak ($I [015]/I [110]$) (Goldsmith & Graf, 1958; Hardy & Tucker, 1988) for all samples with high enough dolomite intensities and lacking significant interference from other mineral reflections. Dolomite CaCO_3 content in mole percentage was semiquantitatively estimated following the equation (Lumsden, 1979): $\text{NCaCO}_3 = 333.33 d - 911.99$, where NCaCO_3 is the mol % CaCO_3 in the dolomite lattice and d is the d spacing in Å of the 104 peak. The position of dolomite 104 reflections was obtained using quartz as an internal standard.

In order to isolate dolomite from aragonite and calcite for stable isotope analysis ground sample material was exposed to 0.27 M disodium ethylenediaminetetraacetic acid (pH 6.3) for 20 min (Geske et al., 2015). The material was subsequently rinsed with distilled water and collected with filter paper where it was left to air-dry at room temperature. Dissolution of aragonite and calcite was confirmed by XRD analysis (Figure S1). After this treatment dolomite was the main carbonate mineral with more than 95% of the relative carbonate composition. Though trace amounts of low-magnesium calcite may have still been present, they would have negligible influence on sample isotopic composition.

Carbon and oxygen isotope analyses were performed in continuous flow mode following standard procedures (Breitenbach & Bernasconi, 2011) using a GasBench II coupled to a ThermoFinnigan MAT 253 mass spectrometer at the Ruhr-University Bochum. Depending on dolomite content, 200 to 1,600 μg of sample powder was weighted into borosilicate glass vials and oven-dried at 104°C overnight. Samples were run at 70°C for 2 hr, together with international standards NBS19, IAEA603, CO8, and ETH-1 (ISO-A; Meckler et al., 2014). All results are normalized against an in-house prepared dolomite standard (Fra-DOL, grain size <100 μm , $\delta^{13}\text{C} = 2.74 \pm 0.05\text{‰}$, $\delta^{18}\text{O} = -2.87 \pm 0.1\text{‰}$ Vienna Pee Dee belemnite), which has been normalized to the dolomite standard (Müller et al., 2004; Spötl & Vennemann, 2003) prepared by Thorsten Vennemann. Results are reported with respect to the Vienna Pee Dee belemnite standard.

Lithological description was performed on high-resolution composite profile images following the previously published lithotypes and their genetic interpretations (Stockhecke, Sturm, et al., 2014).

3. Origin and Occurrence of Dolomite

The Lake Van sedimentary profile retrieved by the International Continental Scientific Drilling Program PALEOVAN project (Litt et al., 2012) at the Ahlat Ridge records the last ~600 kyr in a sequence of carbonaceous clayey silts and volcanoclastics (Stockhecke, Sturm, et al., 2014). This study focuses on the last 150 kyr of the sequence. The carbonate fraction of clayey silts comprises aragonite and low-magnesium calcite (both surface water precipitates), and a poorly ordered (degree of ordering 0.29 to 0.55) and Ca-enriched (calcian) dolomite (53–59 mol % CaCO_3) displaying all ordering peaks required to qualify it crystallographically as dolomite (Figure S1). Calcian dolomite concentration varies between 0 and 85% of the relative carbonate

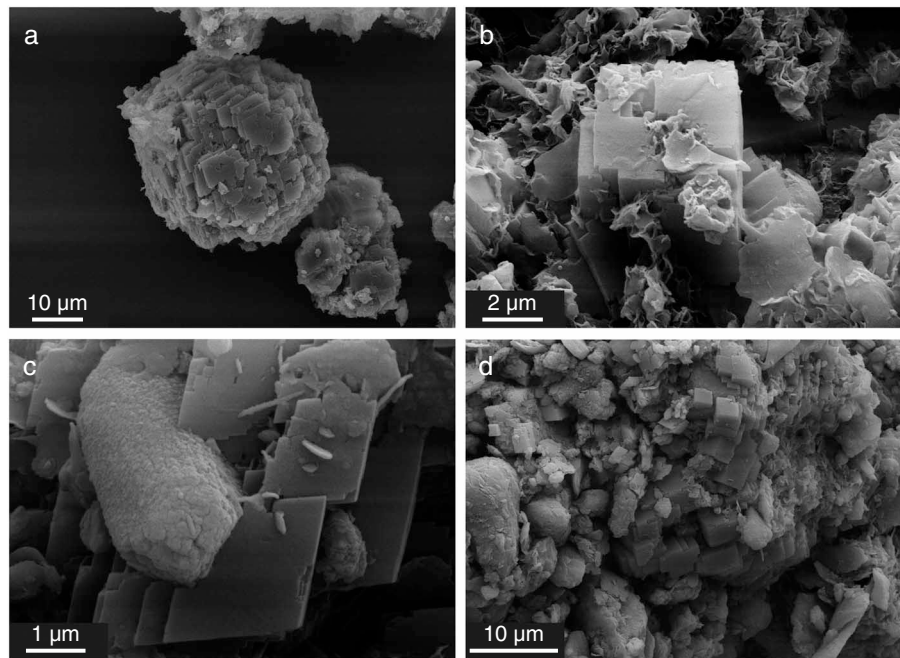


Figure 2. Scanning electron microscopy images of Lake Van dolomite crystals. (a) Large (~40 μm) dolomite crystal from 56.814 to 56.834 mcbf. (b) Dolomite crystal interwoven with clay minerals from 56.814 to 56.834 mcbf. (c) Dolomite growing around a calcium carbonate crystal with notched surface (12.944–12.964 mcbf). (d) Intergrown dolomite crystals with different crystallographic orientations from 12.944 to 12.964 mcbf.

composition (Figure 1) making up to ~60% of the bulk sediment. The concentration of a most likely stoichiometric and possibly detrital dolomite stays at a background level near XRD detection limit (Figure S2, supporting information). Based on several lines of evidence, we conclude that the main portion of Lake Van dolomite is of nondetrital origin. Variation in XRD calcian dolomite peak-intensity is unparalleled by any detrital (siliciclastic) constituent and high dolomite concentrations typically coincide with high X-ray fluorescence Ca/K ratios indicating reduced detrital input (Kwiecien et al., 2014; Figure 1). Enhanced input of siliciclastic material (feldspar and clay minerals) would dilute background carbonate sedimentation and lead to a lower X-ray fluorescence-Ca/K ratio. SEM reveals multiple, well-formed, pristine, euhedral, to subhedral crystal faces (Figure 2), with signs of neither transport nor erosion. Crystals in sizes from ~2 to 40 μm (Figure 2a) are often interwoven with clay minerals (Figure 2b) and individual crystals tend to grow around primary carbonates or merge with different orientations, inferring space-limited precipitation within the sediment rather than precipitation within the water column (Figures 2c and 2d). Morphologically, Lake Van dolomites resemble diagenetic dolomites from Lake Bosumtwi (Talbot & Kelts, 1986), Lake Hayward (Rosen & Coshell, 1992), and a coastal aquifer in Israel (Magaritz et al., 1980). While Lake Van dolomite clearly bears early diagenetic features, at this stage we cannot unambiguously resolve whether it nucleated spontaneously, was driven by a dissolution-reprecipitation process and/or by solid state Ca loss and crystal lattice reordering (potentially via a high-Mg or very high-Mg calcite). The dolomite crystals show no indication of pseudomorphosis after preexisting aragonite or calcite (Figure 2); however, calcium carbonate crystals associated with dolomite often show rough, notched surfaces (Figure 2c), which may be the result of reaction-controlled surface dissolution (Burley & Kantorowicz, 1986).

The most striking feature of dolomite occurrence within the last glacial sediments is its association with finely laminated intervals (Figures 1 and S3). These short-lived intercalations of finely laminated clayey silt are characterized commonly by high total organic carbon, high carbonate, and higher arboreal pollen content. Chronology independent, fine lamination in combination with other proxies indicates deposition under suboxic/anoxic conditions during periods of higher moisture availability and a rising/high lake level (Kwiecien et al., 2014; Stockhecke, Sturm, et al., 2014; Pickarski, Kwiecien, Langgut, et al., 2015). Plotted on the common age model (Stockhecke, Sturm, et al., 2014), the occurrence of high concentrations of dolomite coincides with rapid Northern Hemisphere temperature fluctuations represented as maxima in the NGRIP $\delta^{18}\text{O}$ record (NGRIP, 2004); that is, Greenland Interstadials also dubbed Dansgaard-Oeschger cycles

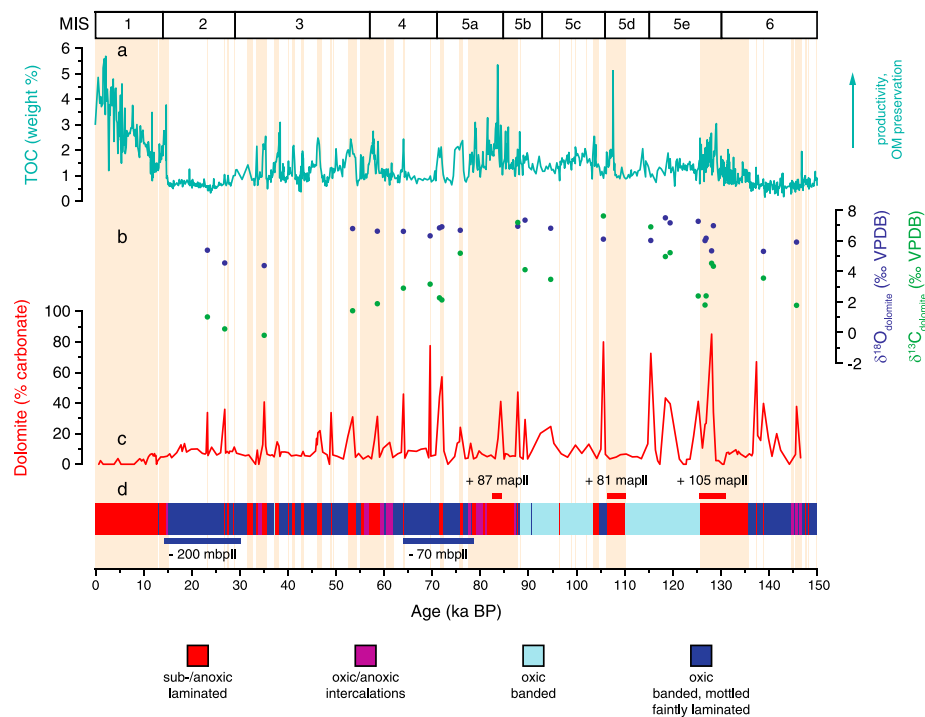


Figure 3. Comparison of dolomite distribution to total organic carbon, lithological facies (Stockhecke, Sturm, et al., 2014), and dolomite $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$. The shaded areas highlight lithologies interpreted as suboxic/anoxic. Within the glacial periods, high (c) dolomite concentrations are restricted to (d) lithological facies interpreted as suboxic/anoxic with typically high (a) total organic carbon. This correlation is not valid for interglacials. Note that (b) $\delta^{13}\text{C}$ varies independently of other proxies (see also Figure S4) and with a higher amplitude than (b) $\delta^{18}\text{O}$ indicating that dolomite $\delta^{13}\text{C}$ is likely influenced by microbial metabolism.

(Figure 1). Similarly, dolomite from the late penultimate glacial period is associated with laminated lithologies (Figures 1 and 3), likely representing Greenland Interstadials (Stockhecke et al., 2016). High dolomite concentrations occur also occasionally within mottled, banded, and laminated clayey silts deposited during Marine Isotope Stage 5 (MIS 5). Noteworthy, sediments deposited at a particularly high lake level $\sim 135\text{--}125$ ka BP (Stockhecke, Sturm, et al., 2014; Tomonaga et al., 2017) contain the highest recorded dolomite concentration (Figure 1). In comparison, the absence of dolomite-rich intervals in the finely laminated, suboxic/anoxic, and organic-rich Holocene sediments is perplexing. Although modern Lake Van water is alkaline and supersaturated with respect to dolomite ($\text{SI}_{\text{Dolomite}} = 3.85\text{--}4.10$) (Reimer et al., 2009), virtually, no dolomite formation occurs.

The occurrence of dolomite-rich intervals in Lake Van during the Pleistocene appears to be mainly confined to intervals characterized by abrupt lithological changes, representing a short-lived lake highstand, succeeded by a lake-level fall. The entire Holocene succession is finely laminated throughout (Figure 1). Consequently, the absence of dolomite within the youngest record may be tentatively explained by the significant lake-level rise at the beginning of the Holocene (Çağatay et al., 2014; Landmann et al., 1996; Stockhecke, Sturm, et al., 2014) and a relatively stable level since (Tomonaga et al., 2017). Based on this observation, we propose that dolomite precipitation may be favored by abrupt changes in pore water chemistry. More precisely, pore water perturbations related to a lowering of the lake level following a highstand, whereas the hypolimnion becomes destratified and/or reventilated, could generate a milieu promoting dolomite formation. Within this scenario early diagenetic dolomite is formed at or closely beneath the sediment-water interface (SWI), as a result of mixing of chemically contrasting lake and pore water (e.g., varying salinity and/or oxygenation). Apparently, minor Holocene lake-level fluctuations (Çağatay et al., 2014) were insufficient in triggering such mixing.

4. Evaluating Factors Controlling Dolomite Formation

Well-constrained, independent, multiproxy records covering the last 150 kyr of Lake Van sediments provide an excellent framework for evaluating the factors commonly viewed as essential in fostering dolomite formation.

Lake-level reconstructions indicate that a maximum fall did not exceed 200 m (Çağatay et al., 2014; Tomonaga et al., 2017), meaning that dolomite at the Ahlat Ridge site must have precipitated at >100-m water depth. Therefore, even if dolomite has formed during falling lake levels, its high $\delta^{18}\text{O}$ values (4.4–7.5‰) (Figures 3 and S4) do not imply evaporative conditions. Instead, the heavy $\delta^{18}\text{O}$ values are an indication of dolomite precipitation at cold temperatures. We tested this hypothesis by simple calculation using the modern Lake Van deep and surface water $\delta^{18}\text{O}$ range (between -0.4 and 1 ‰ VSMOW; Kempe et al., 1990; Jasechko et al., 2013), our measured dolomite $\delta^{18}\text{O}$ range (4.4–7.5‰) and the fractionation factors from Vasconcelos et al. (2005). The resulting possible range of dolomite formation temperatures falls between -5 and 12°C , respectively (see also Table S1). Despite the uncertainties in past water $\delta^{18}\text{O}$ and in dolomite-water fractionation factors (e.g., Murray & Swart, 2017), these values are consistent with modern temperatures below the thermocline ($<4^\circ\text{C}$) (Reimer et al., 2009).

Increased salinity and Mg/Ca ratios are considered key factors for dolomite precipitation and have been used to interpret the presence of dolomite in geological records (Çağatay et al., 2014; Dean et al., 2015; Drummond et al., 1996; Landmann et al., 1996). Although lake-level fluctuations must have affected salinity (and Mg/Ca) of the Lake Van water, two arguments strongly suggest that these factors did not play a crucial role in triggering dolomite formation by directly affecting dolomite kinetics: (1) although at different resolution, there is no correlation between pore water and sedimentary salinity proxies (Randlett et al., 2017; Tomonaga et al., 2017) and dolomite concentration (Figure 1) (i.e., MIS 2–4 characterized by the highest reconstructed salinity coincide with lower dolomite concentration than MIS 5); (2) early diagenetic dolomite-rich intervals occur cyclically in sediments deposited directly prior to a lake-level fall but are virtually absent in sediments representing a low lake level (Figure 1).

The variation in dolomite $\delta^{13}\text{C}$ (-0.2 to $+7.6$ ‰) is significantly larger than the variation in $\delta^{18}\text{O}$ (Figure 3). The $\delta^{13}\text{C}$ of dissolved inorganic carbon (DIC) from a large DIC pools is, unlike lake water $\delta^{18}\text{O}$, relatively insensitive to lake volume changes (Li & Ku, 1997). This fact has an important implication; an additional carbon source must have modified the pore water DIC at the time of dolomite formation. A high range of $\delta^{13}\text{C}$ values for diagenetic carbonates is not uncommon and may be a result from different microbial metabolisms at work (Dimitrakopoulos & Muehlenbachs, 1987). Despite intense research, the exact role of microbial mediation in the mineralization process remains elusive (Bontognali et al., 2010, 2014; Vasconcelos et al., 1995; Wright, 1999). Early studies placed emphasis on the metabolism of sulfate-reducing bacteria, which increases alkalinity and pH (favoring carbonate precipitation), and reduce sulfate (initially considered to inhibit dolomite formation; Petrash et al., 2017; Vasconcelos et al., 1995). Further research showed that the chemistry of the cell surface and microbial by-products such as extracellular polymeric substances (EPS) play a crucial role in dolomite nucleation and can overcome the kinetic barriers that typically prevent the formation of Mg-carbonates at low temperature (Bontognali et al., 2010, 2014; Brauchli et al., 2015; Roberts et al., 2013).

In Lake Van, dolomite is associated with suboxic/anoxic, commonly organic-rich facies in the glacial periods, which is consistent with the hypothesis that microbial metabolism (causing the reducing conditions) and organic matrices (EPS and cells) are essential factors in this mineral formation. Nevertheless, the dolomite content does not always directly correlate with total organic carbon and suboxic/anoxic facies (Figures 3 and S4). Also, if dolomite in Lake Van does precipitate following reventilation of the bottom/pore water, as proposed above, the sediments may have experienced at least temporarily oxic conditions during dolomite nucleation. Furthermore, a microbial metabolism resulting in high alkalinity and pH does not seem to be of key importance due to the inherently high alkalinity (151–156 mmol/l) and pH (9.7–9.9) of the modern lake (Reimer et al., 2009), with essentially no dolomite formation. In contrast, both pH and alkalinity may have even been lower during at least one period of intense dolomite formation. In the entire studied profile only one short interval (equivalent of 126–128 ka BP) contains diatoms (North et al., 2017). The same sediments also contain a substantial concentration of dolomite (Figure 1). Diatoms dwelling in the lakes water are well preserved in the sediment only if the lake pore water is not highly alkaline (Reimer et al., 2009). The presence of biogenic silica in association with dolomite indicates that the latter formed under chemical conditions with pH and alkalinity low enough to preserve diatom frustules.

A variation of the mixing zone model (Badiozamani, 1973) predicting the dissolution of calcium carbonate precursors following hypolimnion reventilation may support high dolomitization rates. Yet such models fail

to explain how kinetic barriers preventing dolomite formation can be overcome (Murray & Swart, 2017). However, the association of dolomite-rich intervals with changing lake levels generally agrees with the dolomitization model of Deelman (1999). This model proposes that fluctuations in pH, temperature, or pressure are capable of breaking Ostwald's step rule, ultimately favoring the stable phase (dolomite) by leaching out the metastable phases (e.g., aragonite). Notably, the possibly minor fluctuations in pH (together with other physico-chemical conditions), following lake-level highstands, are not comparable with the extreme pH variations (~5.3–8.9) in Deelman's experiments. In this case we suggest that similar physico-chemical perturbations of the pore water, which in Deelman's model break Ostwald's step rule, may have affected the microbial community. Carboxyl groups bound to organic matrices and molecules might be particularly effective in catalyzing dolomite formation, via complexing/binding and dewatering Mg ions (Bontognali et al., 2010, 2014; Roberts et al., 2013). The concentration of carboxyl groups produced by a microbial population is not directly proportional to the total biomass. A larger number of carboxyl groups can accumulate when perturbations cause an accelerated cell turnover or death (Roberts et al., 2013) or when changes in water chemistry or redox conditions stimulate microbes to produce larger quantities of EPS to protect themselves against the ecologically unfavorable changing conditions (Petrash et al., 2017). In the case of Lake Van, the changing (falling) lake level accompanied by reventilation and oxygenation of the SWI has likely led to an ecological stress resulting in, for example, increased EPS production or cell mortality. Accordingly, by increasing the concentration of carboxyl groups, these perturbations could facilitate dolomite formation. Assuming that an enrichment in carboxyl groups within the pore waters was a key factor for dolomite nucleation, our data allow us to estimate neither how long these facilitating conditions may have persisted nor whether reestablished anoxic conditions below the SWI or repeated ventilation cycles had an impact in maintaining them.

5. External Forcing of Cyclic Dolomite Formation

The occurrence of early diagenetic dolomite-rich intervals coinciding with Dansgaard-Oeschger events indicates that dolomite formation in Lake Van is, at least in part, controlled by suborbital climate variability. While early diagenetic dolomite precipitation as a result of hydrological changes on orbital (glacial/interglacial) timescales was already suggested for the marine realm (Meister et al., 2008), Lake Van's sediment record provides a compelling argument that dolomite formation within an alkaline environment can be highly sensitive to hydrological changes even on multicentennial timescales. Orbital and suborbitally forced lake-level changes appear to be the ultimate external driving factor and the common denominator for the cyclic occurrence of the dolomite-rich intervals (Figure 1).

6. Implications for Geological Records

Our results demonstrate that in a fluid supersaturated with respect to dolomite, changes in factors commonly assumed important in this mineral formation (with or without precursor phase) such as high temperature, increased Mg/Ca ratio, and increased alkalinity may have no impact on its formation rate. Instead, ultimately climate-controlled lake-level changes and associated ventilation of the lake bottom may modify the sedimentary microbial community. We hypothesize that environmental/ecological stress leading to changes in microbial EPS production might be a key component in facilitating dolomite formation in alkaline environments such as Lake Van.

The cyclic occurrence of dolomite in alkaline Lake Van provides a unique analogue potentially helpful for interpreting Neoproterozoic alkaline oceans and related dolomite formation, which share similar features beyond deposition in an alkaline carbonate saturated environment (Kempe & Kazmierczak, 2003). These include dolomite within finely laminated (Le Ber et al., 2013) and fabric preserving sediments (Hood et al., 2011), its association with deglacial highstand deposits (Hoffman et al., 2007), anoxic conditions (Font et al., 2006), possible cold-water precipitation (Pokrovsky et al., 2010), and cyclic changes between dominance of dolomite and calcium carbonate (Tojo et al., 2007). The comparison between Lake Van's dolomite and ancient dolomite might prove valuable in constraining some of the important issues discussed for cap dolomite formation, such as warm (Nédélec et al., 2007) versus cold (Pokrovsky et al., 2010) water temperatures, oxidation state (Font et al., 2006) and timescales of dolomite formation, and Neoproterozoic deglaciation (Hoffman et al., 2007).

Finally, recognition of early diagenetic dolomite in a deep lacustrine setting (below the thermocline at >100-m water depth) provides an incentive to treat carbonate-based paleoenvironmental reconstructions with caution. The Lake Van example clearly shows that the occurrence of dolomite in a geological record does not necessarily point toward strongly evaporative conditions and consequently does not imply a paralleled increase in water temperature, aridity, salinity, Mg/Ca ratios, alkalinity, or pH. Also, our study demonstrates that a significant contribution of early diagenetic dolomite (up to 60% of the bulk sediment) does not alter the original fabric and preserves the fine lamination. This fact is of particular importance for unlithified sediments recovered from modern lakes, where fine lamination and/or presence of varves is generally considered as an evidence against diagenetic alteration. If unrecognized and unaccounted for, the presence of dolomite will likely bias carbonate isotopic analyses and lead to discrepant comparisons between different proxies (Kwiecien et al., 2014; Pickarski, Kwiecien, Djamali, et al., 2015; Pickarski, Kwiecien, Langgut, et al., 2015) and erroneous interpretations. Consequently, realizing the challenges of environmental association and of overlooking dolomite occurrence is vital for the integrity of carbonate-based paleolimnological and paleoclimatic interpretations.

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